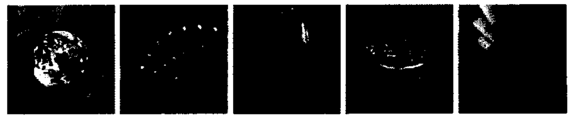

Evaluation of Sediment Remediation Goals For Former Industrial Facilities Claymont, Delaware

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Acronyms and Abbreviations

%	percent
AUF	area use factor
AVS	acid volatile sulfide
BSAF	biota-sediment accumulation factor
CERCLIS	Comprehensive Environmental Response, Compensation, and Liability Information System
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DDx	sum of DDT and its metabolites DDD and DDE
DRBC	Delaware River Basin Commission
EC	effect concentration
EFH	essential fish habitat
ELMR	Estuarine Living Marine Resources
ESB	equilibrium partitioning sediment benchmark
f_{OC}	fraction organic carbon
g/day	grams per day
K_{oc}	organic carbon-water partition coefficient
LC25	lethal concentration to 25% of the test population
LC50	lethal concentration to 50% of the test population
LOEC	lowest observed effect concentration
MCSS	Major Contaminated Sediment Sites
mg/kg	milligram(s) per kilogram
MSA	Magnuson-Stevens Act
µg/gOC	microgram(s) per gram of organic carbon
µmol/gOC	micromol(s) per gram of organic carbon
NOAA	National Oceanic and Atmospheric Administration
NOEC	no observed effect concentration
PCB	polychlorinated biphenyl
RG	remediation goal
SEM	simultaneously extracted metals
TOC	total organic carbon

1 Introduction

This report documents the development and results of a sediment remediation goals (RGs) evaluation conducted in support of the Interim Remedial Measures Workplan being prepared for a nearshore area of the Delaware River adjacent to certain industrial properties located in Claymont, Delaware. Specifically, RGs have been developed for the pesticide dichlorodiphenyltrichloroethane (DDT) and its metabolites (dichlorodiphenyldichloroethane [DDD] and dichlorodiphenyldichloroethylene [DDE]; collectively "total DDx"), arsenic, and lead, following the methodology submitted to the U.S. Environmental Protection Agency (USEPA) on August 15, 2011, as approved by USEPA on August 19, 2011. These RGs consider the following ecological and human health endpoints:

- Sediment toxicity to benthic invertebrates
- Adverse effects on fish due to bioaccumulation in fish and/or invertebrate tissue
- Adverse effects on wildlife due to fish consumption
- Adverse effects on human health due to fish consumption

Sections 2 through 5 of this report address each of these risk endpoints. Precedents for sediment cleanup values for total DDx, arsenic, and lead are also reviewed in Section 6 for comparison to the RGs developed herein.

This report presents a review of published concentration thresholds in sediment that may represent a potential for effects to ecological receptors and gathering of information relating to known conditions in the Delaware River. Based on a comparison of the findings of this review with the available site data, additional targeted sampling is recommended to better define the remedy limits (Section 7).

2 Protection of Benthic Invertebrate Community

This analysis of risk-based sediment concentrations for the protection of benthic invertebrates focuses on cause-effect relationships between DDx, arsenic, and lead concentrations and adverse effects on invertebrates. It is widely accepted in the scientific community that existing sediment quality guidelines for these chemicals do not necessarily reflect cause-effect, concentration-response relationships, and thus that they are not useful for predicting toxicity *due to* the specific chemicals of interest. As an alternative, we review multiple lines of evidence that are suitable for characterizing cause-effect, concentration-response relationships, including:

- Spiked sediment toxicity tests;
- Sediment toxicity and/or benthic community data from sites where DDx, arsenic, or lead is the predominant chemical of concern; and
- Extrapolation of aquatic toxicity data to sediments using USEPA's (1993a, 2005a) equilibrium partitioning approach.

This approach is consistent with USEPA methods for developing cause-effect sediment benchmarks (USEPA 2003a, 2005a). These lines of evidence are discussed and interpreted for each chemical of interest, following an overview of existing sediment quality guidelines and their limitations.

2.1 Existing Sediment Quality Guidelines

Generic sediment quality benchmarks for DDx, arsenic, and lead are intended to protect benthic invertebrates. The evaluation of risks to benthic invertebrates is complicated by the fact that these generic, "empirical" sediment quality benchmarks are of limited utility (as discussed further below) and are generally inconsistent with data suitable for estimating cause-effect, concentration-response relationships for chemical-related sediment toxicity.

Table 2-1 summarizes several generic sediment quality benchmarks for DDT, DDD, DDE, total DDx, arsenic, and lead, as identified from Oak Ridge National Laboratory's online Ecological Benchmark Tool (http://rais.ornl.gov/tools/eco_search.php). This is not a comprehensive list of available sediment benchmarks for the compounds of interest, but it is representative of the most commonly used values. The benchmarks for DDx vary by nearly 3 orders of magnitude, ranging from 0.002 to 0.572 milligrams per kilogram (mg/kg)[1]. The benchmarks for arsenic range from 5.9 to 70 mg/kg, and the benchmarks for lead range from 30.2 to 250 mg/kg. All of the benchmarks shown in Table 2-1 were derived using a family of empirical approaches that relies upon large databases of paired chemical and biological data, compiled from numerous field and laboratory sediment studies.

[1] All sediment concentrations in this report are given on a dry-weight basis, unless otherwise noted.

The derivation of empirical sediment quality guidelines was initiated at a time when little information was available to understand cause-effect, concentration-response relationships for individual chemicals or chemical mixtures in sediment (Engler et al., 2005). It was envisioned in the 1980's that, by accumulating enough data on sediment chemistry and biological responses to different sediments, a pattern would emerge correlating the incidence of biological effects with specific concentrations of specific chemicals in sediment (Long et al., 1995; Engler et al., 2005). It was apparent by the 1990's, however, that this was neither possible nor scientifically defensible (Engler et al., 2005).

Key characteristics of the datasets used to derive empirical sediment quality benchmarks are:

- The sediment samples that populate the data set contain many different chemical contaminants, not only DDx, arsenic, or lead.
- The chemical-specific cause(s) of toxicity observed in different laboratory tests with these sediments are not known.
- The sediments vary in geochemical characteristics which are known to influence bioavailability (e.g., organic carbon content, sulfide concentration).
- Chemical bioavailability was not determined.

These characteristics limit the use of the benchmarks for DDx, arsenic, and lead to serving as indicators of the overall level of sediment contamination (by many chemicals) at the locations included in the data set. They are not reliable indicators of toxicity due to DDx, arsenic, or lead, respectively. This limitation is widely acknowledged by scientists involved in sediment assessments and is applicable to sediment quality benchmarks derived for other contaminants as well (Wenning et al. 2005, Batley et al. 2005).

2.2 Total DDx

For total DDx, extensive information is available from the scientific literature to identify cause-effect, concentration-response relationships between sediment concentrations and toxicity to benthic invertebrates. These relationships are reflected in published sediment toxicity test results, biological data from major DDx sites, and application of the USEPA's (1993a, 2008) equilibrium partitioning approach as described below.

2.2.1 Spiked Sediment Toxicity Tests

Spiked sediment toxicity tests are controlled experiments that can establish cause-effect concentration-response relationships, provided that chemical bioavailability is sufficiently well understood to permit extrapolation among sediments. Results of spiked sediment toxicity tests for DDx are summarized in Table 2-2.

There are limitations to using spiked sediment toxicity tests. Principal among these is that chemical bioavailability in sediment decreases as contact time with the sediment increases. For this reason, spiked sediment toxicity tests tend to overestimate toxicity compared to sediments that have contained contaminants for many years. The equilibration times listed for the spiked sediment studies in Table 2-2 are reasonable and sufficient to avoid gross overestimation of bioavailability, although the tests should be considered conservative with regard to bioavailability. Findings of the spiked sediment studies are summarized as follows:

- The most conservative effects threshold that can be drawn from Table 2-2 is approximately 50 micrograms per gram organic carbon (µg/gOC) (see below). This is equivalent to 0.5 mg/kg DDx for sediment containing 1 percent (%) organic carbon and 2.5 mg/kg DDx for sediment containing 5% organic carbon. As indicated by the results summarized on Table 2-2, *Hyalella azteca* and *Chironomus* spp. are particularly sensitive to DDx.

- Ingersoll et al. (2004) compared 10-day and 42-day survival of *Hyalella azteca* and reported almost identical 25% lethal concentration (LC25) and 50% lethal concentration (LC50) values between the two exposure durations, although reproduction was affected at lower concentrations. Ingersoll et al. (2004) also conducted long-term colonization studies with DDD-spiked sediments, a method that provides more realistic field conditions while controlling sediment chemistry. Reductions in colonization by Chironomid midges (effect concentration [EC]25 = 47 µg DDD/gOC) were observed at concentrations similar to the LC25 and LC50 reported from 10-day toxicity tests (i.e., approximately 50 µg/gOC).

- Many of the spiked sediment toxicity studies have been conducted with freshwater organisms; however, the estuarine amphipod *Leptocheirus plumulosus* is similar in sensitivity to *Hyalella azteca* and *Chironomus* spp.

- Other organisms, such as polychaete worms, freshwater aquatic worms, and mollusks are considerably less sensitive than amphipods and midges to DDx.

2.2.2 Sediment Toxicity at Major DDx-Contaminated Sediment Sites

Table 2-3 summarizes results of sediment toxicity testing and benthic invertebrate community evaluations at major DDx sites. Although it is possible that contaminants other than DDx may have influenced the results of these studies, the likelihood that observed effects were due to DDx is much greater than at sites where DDx is not the major contaminant of interest (such as the sites used to derive empirical sediment quality benchmarks).

- Swartz et al. (1994) reviewed amphipod toxicity test results for sediments from three DDT-contaminated sites (the United Heckathorn Superfund Site in Richmond, CA; a DDT manufacturing site in Huntsville, AL; and the Palos Verde Shelf on the California coast).

    - Amphipod LC50s ranged from 1,040 to 2,600 µg/gOC, higher than the LC50s noted in spiked sediment tests. This range equates to 10.4 to 26 mg/kg for sediment containing 1% organic carbon, and 52 to 130 mg/kg for sediment containing 5% organic carbon.

 - A toxicity threshold of approximately 300 µg/gOC was noted in laboratory tests, and field surveys indicated declines in amphipod abundance at concentrations exceeding approximately 100 µg/gOC. These concentrations are equivalent, respectively, to 3 and 1 mg/kg for sediment containing 1% organic carbon, and 15 and 5 mg/kg for sediment containing 5% organic carbon.

- Ferarro and Cole (1997) assessed benthic invertebrate community composition at the United Heckathorn site and found results for amphipod abundance that are consistent with the 100 µg/gOC threshold identified by Swartz et al. (1994). However, an overall invertebrate index showed differences in community composition at total DDT concentrations as low as 32 µg/gOC (Ferraro and Cole 1997).

- Data from major DDx sites indicate that severe effects on benthic communities can occur at concentrations on the order of 2,000 to 3,000 µg/gOC.

The data shown in Table 2-3 support an effects threshold range of approximately 30 to 300 µg/gOC. This equates to 0.3 to 3 mg/kg for sediment containing 1% organic carbon, and 1.5 to 15 mg/kg for sediment containing 5% organic carbon.

2.2.3 Equilibrium Partitioning Evaluation

The equilibrium partitioning approach allows aquatic toxicity data to be extrapolated to sediment, because extensive testing has shown that sediment porewater concentrations (rather than bulk sediment concentrations) effectively predict toxicity of hydrophobic organic compounds in whole-sediment exposures (USEPA 1993a, 2003a, McDonough et al. 2010, Hoke et al. 1994, Kraaij et al. 2003). Whole-sediment benchmarks are estimated from porewater benchmarks based on sediment-specific organic carbon content and chemical-specific organic carbon-water partition coefficients (K_{oc}). The equilibrium partitioning evaluation included the following steps:

- Updating the USEPA's (1980) compilation of acute aquatic toxicity data for DDT and calculating a Final Acute Value in accordance with USEPA procedures for water quality criteria derivation.

- Identifying an appropriate acute-to-chronic ratio to estimate a Final Chronic Value for DDT.

- Evaluating the relative toxicity of DDD and DDE as compared to DDT.

- Extrapolating the resulting aquatic toxicity benchmarks to sediment, assuming equilibrium partitioning between sediment particles and porewater.

- Determining an equilibrium partitioning sediment benchmark (ESB) for total DDx, based on the site-specific proportion of the total represented by DDT, DDD, and DDE.

The derivation of an ESB for DDx, in accordance with USEPA (1993, 2008) procedures is presented in Appendix A. The total DDx ESB is estimated as 160 µg/gOC. This ESB is within the effects threshold range identified for DDx-contaminated sediment sites (approximately 30 to 300 µg/gOC).

2.2.4 Integration of Lines of Evidence for DDx

The empirical sediment quality benchmarks summarized on Table 2-1 for DDx are generally orders of magnitude lower than can be supported based on the cause-effect data discussed above. This reflects the limitations of the empirical benchmark derivation methods. Several lines of evidence indicate a higher effects threshold is protective of benthic invertebrates at the Site. The data from spiked sediment toxicity tests, major DDx sites, and the equilibrium partitioning approach all support a cause-effect RG on the order of 50 to 160 µg/gOC.

- The most conservative effects threshold that can be drawn from spiked sediment tests is approximately 50 µg/gOC. Spiked sediment toxicity tests tend to overestimate chemical bioavailability, due to limited chemical-sediment contact time.

- The most conservative effects threshold of sediment toxicity testing and benthic invertebrate community evaluations at major DDx sites is approximately 30 µg/gOC. This type of study can be affected by the presence of co-contaminants. By the same token, these studies also implicitly account for any unmeasured DDT metabolites (beyond DDD and DDE) that may have been present.

- The ESB derived for the site is 160 µg/gOC. The partition coefficients used in this estimate are uncertain but more likely to be over-conservative than under-conservative.

Based on these results, **50 to 160 µg/gOC** is identified as the range of risk-based sediment concentrations to protect benthic invertebrates from adverse effects due to DDx.

Several site-specific factors can influence the relationship between DDx exposures and effects on benthic invertebrates. If a more definitive, site-specific evaluation of benthic risks were undertaken, it would likely result in a higher estimated RG, as follows:

- Sediment organic carbon quantity and type can affect DDx bioavailability, with the potential for enhanced sorption to black carbon (Tomaszewski et al. 2007), which in turn, would result in a higher RG.

- The presence of DDT in crystalline form may reduce its bioavailability (Boese et al. 1997), resulting in a higher RG.

- Lastly, if site-specific habitat conditions are not conducive to supporting the most DDx-sensitive species (i.e., even in the absence of DDx), then higher DDx concentrations would be required to affect benthic invertebrate community structure.

Thus, the recommended total DDx concentration of **50 to 160 µg/gOC** is considered adequately conservative and protective of the environment. This equates to 0.5 to 1.6 mg/kg for sediment containing 1% organic carbon, and 2.5 to 8 mg/kg for sediment containing 5% organic carbon.

2.3 Arsenic

The evaluation of cause-effect, concentration-response relationships for arsenic effects on benthic invertebrates is informed primarily by (1) the results of spiked sediment toxicity studies, and (2) sediment toxicity and benthic invertebrate community data for arsenic-dominated contaminated sediment sites. An approach to estimate arsenic partitioning between sediment and porewater has not been developed; rather, arsenic concentrations in porewater are typically measured directly. Therefore, the equilibrium partitioning approach is not applicable for arsenic. However, interpretation of measurements of arsenic in sediment porewater is presented below in the context of spiked sediment study results. The available lines of evidence are presented below, following an overview of factors influencing arsenic bioavailability and toxicity.

2.3.1 Background Information: Arsenic Geochemistry

Arsenic geochemistry and bioavailability are affected by the interaction of several factors, including pH, redox potential, and the concentrations of sulfide, iron, and manganese (Drever 1997; Baumann and Fisher 2011). Arsenic readily converts between As(III) and As(V) depending on ambient redox conditions. This speciation affects mobility and bioavailability but has less influence on the toxicity of the bioavailable fraction. No systematic difference is observed in the relative toxicity of As(III) and As(V) to aquatic organisms, and both species are toxic to humans under chronic exposure scenarios (Smedley and Kinniburgh 2005). However, it is important to note that for the food chain, inorganic arsenic is converted to organic forms, which are much less toxic to humans and wildlife (Neff 1997).

Arsenic is immobilized by sorption to iron and manganese oxides in aerobic sediments, and formation of frequently mixed-phase sulfide compounds in anaerobic sediments (i.e., arsenic may sorb to other precipitating sulfide phases such as iron sulfides). The extent of As(III) and As(V) sorption to iron oxides or other precipitating phases is pH- and redox-dependent (Drever 1997). Arsenic is mobilized at oxic-anoxic boundaries and in sulfide-poor reducing environments. Arsenic is most bioavailable in reducing environments at low pH and least bioavailable under oxic conditions (Drever 1997, Harrison 2007). Arsenic is expected to be less bioavailable in marine or estuarine sediments compared to freshwater sediments, due to the abundance of sulfur in seawater (Neff 1997).

2.3.2 Spiked Sediment Toxicity Tests

Four spiked sediment toxicity studies for arsenic were identified; they provide data for several benthic invertebrate species, forms of arsenic, and types of sediment (Table 2-4). The reported toxicity values are above 100 mg/kg dry weight in all cases. In general, spiked sediment studies are more likely to overestimate rather than underestimate bioavailability of metals relative to field-contaminated sediment. Slow sorption and mineralization processes tend to progressively decrease metal bioavailability in sediments, but in spiked sediment tests, the time elapsed between sediment spiking and exposure of organisms often is not sufficient for these processes to approach field conditions. Findings for the spiked sediment studies are as follows:

- The most conservative lowest observed effect concentration (LOEC) available from arsenic spiked sediment studies is 39 mg/kg from Liber et al. (2011) for an 11% reduction in midge growth compared to the control organisms. Midge growth is ecologically relevant because it serves as an indicator of potential effects on reproductive fitness (Sibley et al. 1997). To quantify the relationship between midge growth and reproductive success, Sibley et al. (1997) manipulated growth of *Chironomus dilutus* (formerly *C. tentans*) by varying feeding rates. Larval weight was predictive of reproductive success and intrinsic rates of population increase, with an effect threshold observed between 1.4 mg and 1.6 mg per organism. Given that fully fed larvae weighed 2.0 mg per organism, an ecologically significant effect threshold for midge growth in this study was approximately a 25% reduction in weight. The LOEC from Liber et al. (2011) is well below this degree of growth reduction and therefore does not provide an appropriate basis for the arsenic RG. The arsenic concentration associated with a 25% reduction in midge growth in this study (170 mg/kg) is considered ecologically significant.

- Excluding the Liber et al. (2011) LOEC, the lowest effect concentration is the midge growth LOEC (130 mg/kg) from Martinez et al. (2006). This value also represents a very small magnitude of effect (12% reduction in larval length and 11% rate of larval deformities). However, absent additional information on the ecological significance of these endpoints, 130 mg/kg is considered a relevant result for developing sediment RGs.
- The LC50 results of Burgess et al. (2007) (80.9-88.8 mg/kg wet weight) appear to be relatively sensitive but are difficult to interpret with precision because (1) the sediment concentrations were reported only on a wet-weight basis, and (2) equilibration of the spiked sediment was apparently minimal, which would result in artificially high bioavailability. Additionally, LC50s are not considered appropriate to establish RGs.
- All remaining endpoints in Table 2-4 are less conservative than those listed above.

The spiked sediment toxicity studies also provide insight into the interpretation of arsenic concentrations in sediment porewater and invertebrate tissue. Cui et al. (2011) spiked sediments with three different arsenic sulfide minerals, which yielded whole-sediment LC50s for the amphipod *Corophium volutator* that varied by approximately a factor of four. However, the corresponding porewater LC50s were essentially constant, as were the tissue-based LC50s. Porewater concentrations were thus a better indicator of bioavailable exposures than were whole-sediment concentrations. However, the porewater LC50s were 4-fold lower than a water-only LC50 for the same species. It is uncertain whether this difference reflects the fact that the water-only test was of a different duration and used different test conditions, or that sediment ingestion contributed significantly to amphipod exposures in the spiked sediment test (Cui et al. 2011).

In contrast, Liber et al. (2011) reported 10-day porewater LC50s for the amphipod *Hyalella azteca* and the midge *Chironomus tentans* that were 17-fold and 6-fold higher, respectively, than the corresponding 4-day water-only LC50s. Based solely on the difference in test durations, one would expect the 10-day LC50s to be lower than the 4-day LC50s, not higher as observed. The finding of relatively high porewater LC50s for arsenic is consistent with studies of arsenic-sulfide complexation. Specifically, dissolved thioarsenate (arsenic sulfide) complexes, which may occur in porewater where sufficient sulfide is present, can exhibit lower toxicity than free As(III) ions (Rader et al. 2004; Planer-Friedrich et al. 2008).

2.3.3 Biological Data at Arsenic-Dominated Contaminated Sediment Sites

Our review identified few arsenic-contaminated sediment sites where arsenic was the primary contaminant of concern. Table 2-5 presents sediment toxicity and/or benthic invertebrate community data for three sites where the study authors considered arsenic the primary contaminant of concern. At two of the sites, no adverse effects on invertebrates were observed at the maximum arsenic concentrations evaluated (approximately 180 to 340 mg/kg). At the third site, where antimony was a co-contaminant, the threshold for adverse effects on the benthic invertebrate community was between 100 and 200 mg/kg arsenic.

2.3.4 Integration of Lines of Evidence for Arsenic

Considerably less information capable of characterizing cause-effect, concentration-response relationships for benthic invertebrates is available for arsenic than for DDx. Nevertheless, the available data consistently show arsenic toxicity thresholds to be above 100 mg/kg. Based on the studies reviewed, a range of **130 to 170 mg/kg** is identified as the risk-based sediment concentrations to protect benthic invertebrates from adverse effects due to arsenic. This RG range is conservative and would over-predict toxicity at the sites considered in Table 2-5.

2.4 Lead

Cause-effect sediment quality benchmarks for lead and other divalent metals have been the subject of extensive USEPA research (USEPA 2005a), as described below. However, the specialized data collection required to apply USEPA's equilibrium partitioning approach for assessing divalent metal toxicity in sediment has not been performed at the site. To provide a causal perspective for evaluating the existing sediment lead data, toxicity test results for spiked sediments and field collected sediments from lead-contaminated sediments are also reviewed.

2.4.1 Existing Equilibrium Partitioning Sediment Benchmarks

The USEPA (2005a) has developed benchmarks for assessing the risk of sediment toxicity due to mixtures of lead, cadmium, copper, nickel, silver, and zinc, based on an understanding of the primary factors controlling the concentrations of these metals in sediment porewater. Whereas total organic carbon (TOC) is recognized as the key factor controlling the bioavailability of hydrophobic organic chemicals in sediment (such as DDx), a key factor controlling the bioavailability of divalent metals is the concentration of acid volatile sulfide (AVS). Thus, if the concentration of AVS is greater than the concentration of simultaneously extracted metals (SEM) in sediment on a molar basis, the metals are not bioavailable and do not cause toxicity (Ankley et al. 1996; USEPA 2005a). This premise has been shown to hold true in toxicity tests of sediments collected from sites contaminated primarily with metals (Hansen et al. 1996).

A refinement of the SEM–AVS approach addresses the role of TOC as a secondary factor controlling the bioavailability of these metals in sediments where SEM concentrations exceed the concentrations of AVS. As described by USEPA (2005a), one can predict with 90% confidence that sediment toxicity will not occur if the organic-carbon normalized concentration of "excess" metals ([ΣSEM-AVS] / fraction organic carbon [f_{OC}]) is less than 130 µmol per gram organic carbon (µmol/gOC). A further refinement also incorporates the role of pH in affecting metal bioavailability (Di Toro et al. 2005). Application of these approaches requires measurement of AVS, as well as SEM concentrations of the target divalent metals.

It follows from the SEM – AVS approach that the toxicity of lead to benthic invertebrates depends in part on the concentrations of other divalent metals in sediment. Lead has a higher affinity for sediment binding phases than zinc, and thus an increase in sediment lead concentrations can cause an increase in zinc bioavailability (Mann et al. 2009).

2.4.2 Spiked Sediment Toxicity Tests

Table 2-6 summarizes the results of nine lead-spiked sediment toxicity studies. The lowest toxicity threshold was observed in a two-generation study of amphipod (*Elasmopus laevis*) reproduction, in which a lead concentration of 234 mg/kg caused a 70% decrease in production of young (Ringenary et al. 2007). However, control survival in this experiment was low, indicating that the results could have been confounded by laboratory artifacts. King et al. (2006) observed approximately a 20% decrease in growth of amphipods (*Melita plumulosa*) exposed to 580 mg/kg lead. In several spiked sediment toxicity studies, the lead toxicity threshold was above 1,000 mg/kg.

Borgmann and Norwood (1999) found that lead concentrations in both amphipod tissue and overlying water were representative of bioavailable exposures. Casas and Crecelius (1994) showed that the SEM-AVS approach and comparison of porewater exposures to water-only toxicity thresholds were generally effective in predicting toxicity of sediments spiked with divalent metals, including lead. However, King et al. (2006) reported porewater lead concentrations that were well below water-only toxicity thresholds in spiked sediments that elicited toxicity due to lead.

2.4.3 Biological Data from Lead-Contaminated Sediment Sites

Sediment toxicity or benthic invertebrate community data for clearly lead-dominated sediment sites were not identified during this evaluation. However, toxicity thresholds for lead from three representative sediment sites are presented in Table 2-7. Two of the studies (Kemble et al. 1994, Hansen et al. 1996) were used by USEPA to validate the SEM-AVS approach (USEPA 2005a). The lead concentrations associated with effects (or lack of effects) in these studies are consistent with the findings of the spiked sediment studies described above. In the most conservative case, the LOEC identified for the Upper Clark Fork River site was 570 mg/kg (Kemble et al. 1994).

In the third study, Borgmann (2003) presents a method to derive cause-effect-based sediment quality benchmarks for metals, based on extensive sediment toxicity and bioaccumulation data from lakes in the vicinity of Sudbury, Ontario, the site of a former smelting operation. The approach relies on tissue-based toxicity thresholds developed for the amphipod, *Hyalella azteca*. Based on metal concentrations in amphipods exposed to area sediments, observed toxicity was determined to be due to metals other than lead. Using site-specific bioaccumulation factors, Borgmann (2003) predicted that a lead concentration of 130,000 mg/kg would be required to elicit 25% amphipod mortality, but this value was well beyond the range of the underlying data. Therefore, Borgmann (2003) identified a sediment quality benchmark for lead as greater than 1,170 mg/kg (the maximum measured lead concentration).

2.4.4 Integration of Lines of Evidence for Lead

The site-specific toxicity of lead in sediment depends on a variety of factors, such as the concentrations of sulfide, TOC, pH, and other divalent metals. For this reason, spiked sediment toxicity tests and tests of field-contaminated sediments representing a range of species and sediment types have yielded a wide range of toxicity thresholds for lead. In the most sensitive of the tests reviewed, toxicity was observed at a concentration above 200 mg/kg; control survival in this test was low. In all other cases, toxicity was observed only at concentrations above 500 or 1,000 mg/kg. For the purposes of determining whether lead is a risk driver at the Delaware River site, **570 mg/kg** (based on the results of Kemble et al. 1994) is identified as the risk-based sediment concentration to protect benthic invertebrates from adverse effects due to lead.

3 Protection of Fish

To determine whether fish exposures to site sediments may represent a significant pathway at the site, protective sediment concentrations of total DDx, arsenic, and lead were back-calculated using published bioaccumulation factors and toxicity reference values. The resulting risk-based concentrations are considered adequately conservative based on the selection of input factors.

3.1 Representative Species

Representative species were selected to evaluate protective sediment concentrations for the site. The selected species include those predicted to be most susceptible and likely to inhabit the site, and thus protective of other, less susceptible species. Differences in key exposure parameters, such as area use factors (AUF) and lipid content, were considered during selection of these representative species. The site is located at the far upstream end of the saline mixing zone within the Delaware Estuary, where the river is inhabited by a mixture of saline-tolerant freshwater species and freshwater-tolerant estuarine species.

National Oceanic and Atmospheric Administration's (NOAA's) Estuarine Living Marine Resources (ELMR) Program (1994) documents important fish and invertebrate species in the nation's estuaries as determined by commercial value, recreational value, indicator species of environmental stress, and ecological value. Among these species, those listed as abundant to highly abundant in the Delaware Bay Estuary include: American eel (*Anguilla rostrata*), blueback herring (*Alosa aestivalis*), alewife (*Alosa pseudoharengus*), American shad (*Alosa sapidissima*), Atlantic menhaden (*Brevoortia tyrannus*), bay anchovy (*Anchoa mitchilli*), various killifishes (such as mummichog) and silversides, white perch (*Morone americana*), bluefish (*Pomatomus saltatrix*), weakfish (*Cynoscion regalis*), spot (Leiostomus xanthurus), windowpane flounder (Scophthalmus aquosus), hogchoker (*Trinectes maculatus*), American oyster (*Crassostrea virginica*), northern quahog (*Mercenaria mercenaria*), softshell clam (*Mya arenaria*), daggerblade grass shrimp (*Palaemonetes pugio*), sevenspine bay shrimp (*Crangon septemspinosa*), and blue crab (*Callinectes sapidus*).

Among the other considerations for representative species of the site are those species federally managed under the Magnuson-Stevens Act (MSA). Under the MSA, NOAA Fisheries, in cooperation with regional fishery management councils, identify Essential Fish Habitat (EFH) of federally managed species to (1) minimize threats to these habitats caused by certain fishing practices and coastal and marine development; and (2) restore or conserve existing habitat. However, no EFH is found within the immediate vicinity of the Site. The closest designated EFH is identified within Delaware Bay and includes habitat for windowpane flounder, winter flounder (*Pseudopleuronectes americanus*), bluefish, Atlantic butterfish (*Peprilus triacanthus*), summer flounder (*Paralichthys dentatus*), scup (*Stenotomus chrysops*), black sea bass (*Centropristis striata*), king mackerel (*Scomberomorus cavalla*), Spanish mackerel (*Scomberomorus maculates*), and cobia (*Rachycentron canadum*).

In addition, ENVIRON submitted inquiries to appropriate state and federal authorities regarding the presence of threatened and endangered species in the vicinity of the site.

- The U.S. Fish and Wildlife Service indicated that proposed or federally listed endangered or threatened species are not known to exist within the project impact area.

- The Delaware Department of Natural Resources indicated that this portion of the river is utilized by Atlantic sturgeon (*Acipenser oxyrinchus*), a species of local and regional concern and a NOAA National Marine Fisheries Service "candidate species," and the federally endangered short-nosed sturgeon (*Acipenser brevirostrum*). Additionally, striped bass (*Morone saxatilis*) spawn in the vicinity and American shad (*Alosa sapidissima*) pass through the area during upstream migration in April through June. Striped bass and American shad are not listed species, but are considered important recreational and commercial resources, and the shad is a species undergoing restoration efforts.

- The Natural Diversity Section of the Pennsylvania Fish and Boat Commission indicated that the state threatened eastern redbelly turtle (*Pseudemys rubriventris*) exists in the vicinity of the project site. However, the Commission concluded that the project site habitat is not suitable for redbelly turtles.

- The Pennsylvania Department of Conservation and Natural Resources indicated that that no species or resources of concern under the Department's jurisdiction are known occur in the vicinity of the project.

Final considerations for representative species include availability of data necessary to develop sediment concentration modeling equations. Due to human health concerns, a large amount of data that has been utilized to develop Fish Consumption Advisories is publicly available (see Section 5.1). Among those species frequently collected are Amercian eel, white perch, channel catfish (*Ictalurus punctatus*), common carp (*Cyprinus carpio*), and striped bass (*Morone saxatilis*).

Based on the above considerations, the following three representative species were selected for the evaluation of RGs, as follows:

- Mummichog (*Fundulus heteroclitus*). A small fish that feeds primarily on detritus and invertebrates, the mummichog is selected for evaluation because its small home range (observed as 36 meters along stream banks; Lotrich 1975) maximizes potential exposure to site sediments

- White perch (*Morone americana*). The white perch is selected to represent medium-sized fish, based on its relatively high lipid content and the availability of information on its movement patterns. Like most fish species, white perch use of the site is expected to be transient. White perch are omnivorous and may be both prey for wildlife and food for humans (in the absence of fish consumption restrictions).

- Channel catfish (*Ictalurus punctatus*). Channel catfish are relatively large, omnivorous fish that might be targeted by anglers, but for the fish consumption advisory in effect for the Delaware River (see Section 5.1). Their relatively high lipid content in both whole fish and edible portions and the moderate extent of their movements (compared to anadromous species, for instance) promote a relatively high exposure potential.

Specific assumptions regarding these species' lipid content and area use are summarized in Tables 3-1 through 3-3. It should be noted that this evaluation of AUFs did not account for the tidal nature of the site, which would reduce exposure of fish to the nearshore areas in portions of the study area.

3.2 Total DDx

Two lines of evidence are available to evaluate total DDx sediment concentrations for protection of fish. First, the equilibrium partitioning evaluation described in Section 2.2.3 and detailed in Appendix A involves extrapolation of aquatic toxicity data to sediment porewater. The aquatic toxicity data set includes extensive data for fish. Mummichog are a benthic fish (bottom-dwelling), and at times they burrow in sediment, where they would be exposed to porewater. However, most of their water exposure is above the sediment surface, and exposures to DDT in the water column are diluted compared to DDT concentrations in porewater. The use of estimated porewater concentrations rather than water column concentrations thus tends to bias the ESB toward over-protection. There is some potential that due to food web exposure, fish might encounter greater total DDx exposures than would be estimated based on equilibrium partitioning from sediment to porewater. However, Jarvinen et al. (1977) evaluated effects of DDT on fathead minnows subjected either to aqueous exposures or to both aqueous and dietary exposures. The addition of a dietary exposure pathway increased the magnitude of effects and tissue residues only moderately (i.e., 10% to 2-fold increase). Further, fish are not the most sensitive species to DDT (see Appendix A), such that an ESB derived using both fish and invertebrate data incorporates a margin of safety for fish. Considering all of these factors, the ESB of 160 µg/gOC derived for protection of benthic invertebrates is also protective of fish.

Information linking total DDx concentrations in fish tissue to adverse effects on fish provides another line of evidence for consideration. The conceptual approach to applying this information entails the following steps:

- Identifying a tissue-based toxicity reference value based on published studies linking whole-body fish tissue concentrations and toxic effects.
- Identifying species-specific exposure factors, including whole fish lipid content and AUFs (i.e., percent of time spent in the area affected by the site).
- Integrating the species-specific exposure factors with chemical-specific bioaccumulation factors to predict a total DDx concentration in sediment that would result in fish tissue concentrations equal to the toxicity reference value.

Beckvar et al. (2005) identified several studies linking DDx bioaccumulation to effects on fish; all original studies were reviewed for this report. Only studies measuring DDx in adult fish were considered, because the bioaccumulation factors identified for DDx apply to adult fish, as described below. Tissue-based toxicity reference values from early life stage tissue measurements (e.g., egg concentrations) are not comparable to DDx concentrations in adult fish tissue (Beckvar et al. 2005). However, the studies providing adult fish toxicity thresholds do account for effects on early life stages. Specifically, parent fish tissue concentrations are evaluated based on effects on their offspring.

Among the studies reviewed by Beckvar et al. (2005), several were judged inappropriate for identifying sediment RGs, for the following reasons:

- Although classified as an adult life stage study by Beckvar et al. (2005), Berlin et al. (1981) actually evaluated effects on fry. Also, that study used DDE, which is only a minor component of total DDx at this site.

- Butler (1969) conducted two trials of DDT toxicity to pinfish, in which the fish were given feed containing similar DDT concentrations (4.07 versus 4.70 mg/kg). In one trial, the lowest effect concentration in fish was 0.55 mg/kg, associated with 44% mortality after 10 days exposure. In the other trial, the lowest effect concentration was 5.62 mg/kg, associated with 35% mortality after 21 days. With an order of magnitude difference between the lowest effect concentrations in the two trials, these results clearly were not reproducible.

- Davy et al. (1972) evaluated goldfish behavior in response to DDT exposure by measuring the time between turns during swimming. The relevance of this endpoint is questionable. Further, this was a short-term exposure (4 days). Such acute exposures are not preferred for establishing bioaccumulation-toxicity relationships, because (1) tissue concentrations are not at equilibrium with exposure media, and (2) acute effects may occur through different mechanisms than chronic effects.

The remaining studies reviewed by Beckvar et al. (2005) are appropriate and relevant to the identification of sediment RGs. Each study is reviewed below, and the results are then considered together to identify a toxicity reference value for DDx in fish.

- Macek (1968a) examined the effects of DDT exposure on brook trout growth, finding a significant increase in weight gain in fish exposed to DDT for 31 weeks. This effect is not adverse. The associated total DDx concentration was 13.8 mg/kg in whole fish. Using the same species, Macek (1968b) observed statistically significant, but only slightly higher, mortality of fertilized eggs and fry compared to the control (6.5% in exposed fish versus 2.5% in the controls), when parent brook trout were fed DDT at a rate of 1.0 mg/kg per week. The corresponding, unbounded lowest effect concentration is 2.9 mg/kg in whole adult fish (duplicates are averaged). Fry survival is thus a more sensitive endpoint than juvenile growth for this species. Considering the very small magnitude of the observed effect, a whole fish DDx concentration of 2.9 mg/kg appears very close to (and perhaps somewhat below) a biologically significant effects threshold for brook trout.

- Allison et al. (1963) exposed cutthroat trout to DDT episodically in either food or water and measured tissue concentrations at several points during the exposure period. Fish with tissue residues of 0.6 to 3.9 mg/kg DDx exhibited no significant effects on adult survival, reproduction, or survival of fry. Fish containing 1.7 to 14.1 mg/kg DDx (measured after 166 days of exposure) exhibited significant effects on these endpoints (Allison et al. 1963). Depuration via spawning may account for the reduced body burden (1.7 mg/kg) observed in Lot IV after effects were noted earlier in the study at a higher tissue concentration (3.0 mg/kg). In order to best bracket the critical effect threshold, no-effect and lowest-effect concentrations were calculated from the lot displaying no effects at the highest tissue residue concentrations (Lot IX) and the lot displaying effects at the lowest tissue residue concentrations (Lot IV). The average tissue residue for Lot IV was 3.5 mg/kg, including residues measured near the time the effect was first observed at 6 months (Day 166) until study termination (Day 497). The average tissue residue for Lot IX, calculated for the same time frame, yields a no-effect concentration of 2.8 mg/kg.

- Buhler et al. (1969) examined the effect of varying dietary combinations of p,p'-DDT and technical DDT on survival of chinook and coho salmon fingerlings over 40-, 65-, and 95-day exposure periods. Beckvar et al. (2005) reported effects residues for chinook salmon fed DDT rations for 40 days (Trial I). However, the tissue residue analysis for this trial occurred on Day 7, yielding a short-term exposure tissue residue inappropriate for TRV derivation. A more appropriate effects residue can be taken from Trial II, where fish were fed DDT for 65 days and tissue residue analysis occurred at 11, 40, and 65 days. The lowest effect concentrations for Trial II are 12.1 mg/kg for 40 days of exposure and 12.3 mg/kg for the 65-day exposure. The no effect concentrations are 11.4 mg/kg and 6.60 mg/kg, respectively. The results of Trial II, conducted with chinook salmon, are more conservative than those identified for coho salmon in a similar trial (Trial V).

- Jarvinen et al. (1976 and 1977) reported effects on adult fathead minnows and their progeny for several combinations of food and water exposures. An increase in adult mortality was observed in fish exposed to 0.5 µg/L DDT in water and fed DDT-exposed clams. The average tissue residue calculated for this exposure regime from the time equilibrium was reached (28 days) to study termination (266 days) was 92.8 mg/kg. The average tissue residue for the treatment group in which no effect was observed was 35.8 mg/kg. Fry mortality patterns mirrored those for adult mortality, although the results were not statistically significant. Reduced egg hatchability was reported as a less sensitive endpoint. From this study, fathead minnow is the least sensitive species tested.

Among these studies, Macek (1968b) and Allison et al. (1963) provide the most conservative basis for a fish tissue toxicity reference value for DDx. These studies yield nearly identical estimates of toxicity thresholds for fry survival in brook trout and cutthroat trout, as well as adult mortality in cutthroat trout. The no-effect concentration of 2.8 mg/kg in cutthroat trout is selected as a conservative toxicity reference value to derive a sediment RG.

Bioaccumulation of DDx in fish was estimated from a fish tissue monitoring survey of the Delaware River Basin (Romanok et al. 2006) (Appendix B). Tissue samples collected for organics analysis were composites of 4 to 9 similarly sized adult whole fish. Total length of the fish ranged from 185 to 399 millimeters, and weight ranged from 72 to 766 grams. An average biota-sediment accumulation factor (BSAF) was calculated for total DDx in Delaware Basin fish, for sediments containing more than 10 µg/kg total DDx. Sediments containing lower DDx concentrations were excluded, because non-detectable concentrations introduced excessive uncertainty in BSAF estimates. The resulting BSAF is 2.20 (based on sediment concentration normalized to organic carbon and fish tissue concentrations normalized to lipid). An alternative BSAF source (Wong et al. 2001) yields a virtually identical BSAF (2.22), when a weighted average of median BSAFs for 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE is calculated based on the site-specific composition of total DDx (39.9% DDT, 52.9% DDD, and 6.6% DDE on average). Bioaccumulation of DDx during time spent outside the site was estimated based on median sediment concentrations for the Delaware River basin (Romanok et al. 2006).

The derivation of risk-based DDx concentrations in sediment to protect fish, using the bioaccumulation-based approach, is provided in Tables 3-1 through 3-4. The most sensitive fish species to site-related chemical exposures is the mummichog, because its home range is similar in size to the area of sediment thought to be affected by the site. A sediment DDx concentration protective of mummichog is estimated as 50 µg/gOC. Considering this value and the ESB discussed above, **50 to 160 µg/gOC** is identified as the range of risk-based sediment concentrations to protect fish from adverse effects due to DDx. This equates to 0.6 to 1.6 mg/kg for sediment containing 1% organic carbon, and 2.8 to 8 mg/kg for sediment containing 5% organic carbon. These concentrations are applicable to surface-weighted average concentrations in site sediment following remediation and do not represent "not-to-exceed" values.

3.3 Arsenic

For arsenic, an approach similar to the tissue-based analysis described above for DDx was adopted, with one modification. Specifically, a toxicity reference value based on prey tissue concentrations rather than fish tissue concentrations was used. The toxicity reference value was derived from a study of fish reproductive output when fed polychaete worms from a metals-contaminated site and a clean reference site (Boyle et al. 2008). Specifically, the toxicity reference value was derived as the geometric mean of no-effect and lowest-effect arsenic concentrations (15 mg/kg and 136.5 mg/kg, respectively) in polychaetes (*Nereis diversicolor*) consumed by fish in this fish reproductive toxicity test. This study was preferred over studies linking fish tissue arsenic concentrations to adverse effects, because such studies did not evaluate reproductive endpoints (which are typically sensitive). A sediment-to-invertebrate bioaccumulation factor was used to estimate the arsenic sediment concentration that would result in an invertebrate tissue concentration equal to the target prey concentration for protection of fish.

Tables 3-1 through 3-4 detail the derivation of a risk-based, fish-protective sediment concentration for arsenic. The risk-based concentration for mummichog is approximately **300**

mg/kg. This concentration is applicable to surface-weighted average concentrations in site sediment following remediation, and does not represent a "not-to-exceed" value.

3.4 Lead

For lead, a risk-based sediment concentration to protect fish is back-calculated from a fish tissue toxicity reference value, using the same approach described in Section 3.2 for DDx. Although applicable data are limited for lead, a multi-generation study using brook trout provides relevant information for assessing lead concentrations in fish. Holcombe et al. (1976) observed spinal deformities and reduced growth at a water concentration of 119 µg/L, but not at 58 µg/L, with corresponding whole-body residues of 4.0 to 8.8 and 2.5 to 5.1 mg/kg wet weight, respectively (as cited in Jarvinen and Ankley 1999). A toxicity reference value of 4 mg/kg in fish tissue is adopted for this analysis, because it is the low end of the LOEC tissue concentration range and is also within the NOEC tissue concentration range. A bioaccumulation factor for lead in fish is estimated as described in Appendix B. As shown in Tables 3-1 through 3-4, these values yield a sediment concentration to protect mummichog of **150 mg/kg.** This concentration is applicable to surface-weighted average concentrations in site sediment following remediation and does not represent a "not-to-exceed" value.

4 Protection of Birds

Potential risks to birds are quantitatively evaluated in this section for total DDx and lead, but not for arsenic. Wildlife consumers of fish are typically at low risk due to arsenic, because arsenic in fish tissue is primarily present in nontoxic forms (Neff 1997). As demonstrated by Greene and Crecelius (2006) for the Delaware Estuary, arsenic in shellfish also is primarily present in organic (nontoxic) forms. Avian tolerance for organic arsenic is further evidenced by the fact that farmers have intentionally used organic arsenic (roxarsone) as an additive in poultry feed for many years.

For total DDx and lead, the calculation of risk-based sediment concentrations to protect birds is complex. For example, each bird species consumes multiple prey types, each with different bioaccumulation characteristics, and AUFs must be considered both for the birds and their prey. Therefore, "forward" risk calculations are used to determine whether birds are likely risk drivers for the site. For DDx, avian risks were estimated assuming a site sediment concentration equal to the low end of the total DDx concentration for protection of benthic invertebrates (i.e., 50 µg/gOC). For lead, less information is available to propose a risk-based sediment concentration for benthic invertebrates; therefore, the average measured lead concentration in site sediments was used for risk calculation purposes. If no risks are predicted based on these sediment concentrations, then birds are not significant risk drivers at the site.

The following subsections describe the selection of representative bird species for evaluation, followed by a description of modeled risk estimates and a review of osprey monitoring results for the Delaware Estuary.

4.1 Representative Species

The portion of the Delaware River potentially affected by the site lies toward the downstream end of an area of intensive industrial and urban development. There are few terrestrial features that would attract birds to the immediate vicinity of the site. Among bird species known to breed in northeastern Delaware,[2] the double-crested cormorant (*Phalacrocorax auritus*) and osprey (*Pandion haliaetus*) are the aquatic-feeding bird species most likely to tolerate the urbanized conditions in the vicinity of the site. Osprey nests upstream and downstream of the site have been monitored for reproductive success (Toschik et al. 2005). Both of these fish-eating species are included in this evaluation. In addition, the common merganser (*Mergus merganser*) is included in the evaluation, to represent avian consumption of invertebrates as well as fish.

4.2 "Forward" Risk Calculations

To assess the potential significance of sediment concentrations of DDx and lead, the hypothetical risks to birds were calculated as described below; details of the risk calculations for birds are provided in Tables 4-1 through 4-4.

[2] http://www.pwrc.usgs.gov/bba; http://www.dosbirds.org/statelist?opt=Full+List

- As described above, risks were estimated assuming a sediment total DDx concentration of 50 µg/gOC (based on the benthic screening values identified in Section 2) and a lead concentration of 228 mg/kg (based on the average measured concentration in Delaware River sediment samples collected for the site).

- Total DDx and lead concentrations in prey were estimated using bioaccumulation factors (Tables 4-1 and 4-2; Appendix B) following the same methods used in the calculation of risk-based sediment concentrations to protect fish. Fish prey were represented by mummichog and white perch.

- The daily intake of total DDx and lead by each bird species was estimated based on the concentrations in prey and the birds' food ingestion rates, body weights, and AUFs (Table 4-3).

- The estimated daily intakes were compared to conservative no-effect toxicity reference values from USEPA (2005b, 2007), with the result expressed as hazard quotients (Table 4-3). A hazard quotient of 1 or less indicates that exposures are less than or equal to a no-effect level, and no significant risks are expected.

- The hazard quotients are sensitive to the estimated AUFs. Although the site's small size and urbanized character suggest an AUF on the order of 5%, information to estimate species-specific AUFs is limited. Therefore, a sensitivity analysis was conducted to test the change in risk estimates over a range of AUFs (Table 4-4).

This analysis shows that, for sediment concentrations of 50 µg/gOC DDx and 228 mg/kg lead, double-crested cormorants, osprey, and common mergansers would not be at risk even assuming a conservative, but unrealistic, AUF as high as 100%. Thus, **hypothetical risks associated with exposure of birds to the site are not significant**.

4.3 Osprey Monitoring Results

In 2002, Toschik et al. (2005) measured chemical concentrations in osprey eggs and evaluated reproductive success for 39 nests in the Delaware River and Bay. The study area was subdivided for data analysis purposes; the area that includes the Delaware Valley Works site encompassed osprey nests upstream and downstream of Philadelphia, PA and New Castle, DE and was termed the "north segment." Concentrations of DDE—the DDT metabolite linked to eggshell thinning—were significantly elevated in eggs from the north segment compared to the central and south segments, averaging 1.77 mg/kg wet weight. However, the observed concentrations were below levels associated with eggshell thinning in osprey of 15% to 20% (4.2 to 41 mg/kg wet weight); this degree of eggshell thinning is the typical threshold for egg breakage (Blus 1996, Toschik et al. 2005). Toschik et al. (2005) observed that 9 of 12 eggs from the north segment contained DDE concentrations "within the 95% confidence interval associated with 10 to 15% eggshell thinning." It is uncertain whether this degree of eggshell thinning is associated with population-level effects, although 15% thinning has been suggested as an effect level (Blus 1996). Further, no correlation between DDE concentrations and eggshell thickness was observed (Toschik et al. 2005).

According to Toschik et al. (2005), "nest success and productivity in the Delaware River and Bay study regions generally were similar and fell within the range estimated to maintain a stable osprey population." The authors also characterized productivity within the north segment (1.00 fledglings per active nest) as "marginal to maintain the population," but this statement is difficult to reconcile with the cited productivity range estimated to maintain a population for ospreys on the east coast of the United States (0.80 – 1.15 fledglings per active nest) (Toschik et al. 2005). Regional osprey monitoring results are thus consistent with the risk calculations discussed in Section 4.2.

Toschik et al. (2005) noted three instances of failed nests in which egg concentrations of DDE were at the higher end of the range of observed concentrations. These nests were widely distributed geographically (i.e., one nest each in the vicinity of Trenton, New Castle, and Dover Air Force Base). These findings are consistent with the status of DDx as a widespread environmental contaminant; the data set from the Delaware Valley Works demonstrates localized DDx concentrations with DDE (the metabolite linked to eggshell thinning) as only a minor component. Nevertheless, the sediment remedy proposed for the site will provide for a reduction in potential exposures to DDx, consistent with regional goals of further reducing DDx exposures and promoting population growth for osprey.

5 Protection of Human Health

A risk-based sediment concentration for protection of humans consuming fish from the Delaware River was developed for total DDx only. Fish consumption advisories for the Delaware River in the vicinity of the site indicate that DDx in fish tissue could potentially be of concern, but that arsenic and lead are not of concern with regard to fish consumption. Fish advisory information is discussed below, followed by a description of the derivation of a risk-based sediment concentration for total DDx.

5.1 Existing Fish Consumption Advisories and Fish Tissue Monitoring Data

The site's proximity to the tri-state border of Delaware, Pennsylvania, and New Jersey, the tidal character of the estuary, and the high mobility of certain fish species expected to use the site necessitate the consideration of fish consumption advisories from all three states. While some shared data and conclusions from the Delaware Estuary lead to equivalent advisories among states, other datasets and conclusions result in disparate advisories.[3] Delaware and New Jersey share a "no consumption" advisory for all finfish from the Delaware-Pennsylvania-New Jersey state border to the Chesapeake and Delaware Canal. Delaware specifically identifies polychlorinated biphenyls (PCBs), dioxin, mercury, and chlorinated pesticides as the chemicals of concern.

Immediately upstream of the Site, Pennsylvania has issued a no consumption advisory for American eel and carp due to PCBs and a one meal per month advisory for white perch, channel catfish, flathead catfish, and striped bass due to PCBs; the specified area includes the Delaware River from the Trenton, NJ-Morrisville, PA bridge to the Pennsylvania-Delaware border. For the same general area, New Jersey varies the species list, applies two consumption groups (i.e., general population and high risk individual), and presents a variety of consumption rates. Largemouth bass and hybrid striped bass have no restrictions among the general population, but high risk individuals are advised to consume no more than one meal per week. For American eel and channel catfish, the general public is advised to consume no more than one meal per year, but no consumption is advised for high risk individuals. For white catfish, the general public is advised to consume no more than one meal per month, but no consumption is advised for high risk individuals. For striped bass and white perch, the general public is advised to consume no more than four meals per year, but no consumption is advised for high risk individuals.

The Delaware Department of Natural Resources has determined that fish consumption advisories are not warranted for arsenic in the Delaware Estuary (Greene and Crecelius 2006). Arsenic in fish tissue is present primarily in organic forms (notably arsenobetaine), which are metabolically inert, and thus essentially nontoxic (Neff 1997). Greene and Crecelius (2006) sampled both fish and shellfish from the Delaware Estuary, including a sample location near the

[3] http://www.dnrec.delaware.gov/fw/Fisheries/Documents/Delaware_Fish_Advisory_Chart.pdf; http://www.fish.state.pa.us/fishpub/summary/sumconsumption.pdf; http://www.state.nj.us/dep/dsr/fishadvisories/statewide.htm

site. Tissue concentrations of potentially toxic inorganic arsenic were consistently very low, indicating that arsenic poses no significant risk to consumers of fish and shellfish.

The Delaware Fish Contaminants Committee (2005) did not identify any fish consumption advisory trigger values for lead, indicating that lead in edible fish tissue is not perceived as a human health concern. This is consistent with fish tissue data collected by Meador et al. (2005), who generally found detectable lead concentrations in fish liver and stomach tissue, but not in muscle tissue.

Communication with state agencies was initiated and an internet search was conducted to identify existing and readily available tissue monitoring data for the Delaware Estuary, specifically including the immediate vicinity of the site. The Delaware River Basin Commission (DRBC) (www.state.nj.us/drbc/fishtiss.htm) was identified as a key source of existing data dating back to the 1960s. While these data provided a good indication of representative species for the Delaware Estuary, the few samples collected in the vicinity of the site were quite dated. Therefore, a modeling approach was used to estimate total DDx concentrations in fish and crab that people might consume.

5.2 Back-Calculation of Protective Sediment DDx Concentration

The approach used to calculate concentrations of DDx in sediment that are within the acceptable risk range for the protection of human consumers of fish and crab is analogous to the methods described in Section 3 for protection of fish. At USEPA's request, potential human exposure to site-related chemicals is evaluated for consumption of blue crab, as well as fish consumption. The method used to back-calculate human health-protective sediment concentrations is summarized as follows:

- A target tissue concentration of DDx in fish or crabs was identified, using equations from USEPA's (2000) *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (Table 5-1). The fish (and crab) ingestion rate was selected as 17.5 g/day (USEPA 2000, DRBC 2010).[4] Interviews conducted with anglers who consume fish from the lower Delaware Estuary confirm that the selected fish ingestion rate is conservative (DRBC 2010).

- Channel catfish was selected as the target fish species, for the reasons described in Section 3.1. Parameters to estimate DDx bioaccumulation in channel catfish are shown in Table 5-2.

- Parameters to estimate DDx bioaccumulation in blue crab are shown in Table 5-3. The AUF for blue crab is based on a 20 km range; however, information to estimate an AUF for this species is limited. Thus, an alternative assumption, i.e., that the blue crab's

[4] This approach yields a target tissue concentration that is essentially identical to the lowest DDx concentration that would trigger a fish consumption advisory (Delaware Fish Contaminants Committee 2005), when corrected for the selected fish ingestion rate.

range is more similar to the channel catfish (i.e., approximately 5 km), is also evaluated below.

- Exposure parameters for ingestion of channel catfish and blue crab were integrated with bioaccumulation factors, to calculate the concentrations of DDx in sediment that would result in risk estimates within the acceptable risk range.

The derivation of risk-based total DDx concentrations in sediment for protection of human health is presented in Tables 5-1 through 5-3. The resulting risk-based concentrations in sediment at a target cancer risk of 10^{-5} are 40 µg/gOC total DDx based on channel catfish consumption and approximately 2,000 µg/gOC based on consumption of blue crab. Assuming a lower home range for blue crab of 5 km (similar to the catfish) would yield an alternative risk-based sediment concentration of 500 µg/gOC. Fish consumption is thus a more conservative basis than crab consumption for deriving sediment RGs.

As described above, the initial calculation of the risk-based concentrations is based on a target cancer risk of 10^{-5}. However, as described in rulemaking published by USEPA (61 FR 19432, May 1, 1996; EPA 1996), risk-based media cleanup standards are considered protective if they achieve a level of risk which falls within the 10^{-6} to 10^{-4} risk range. The upper end of this range is also typically considered a threshold for remedial action. Following the methodology described above, this translates into a risk-based concentration ranging from 40 to 400 µg/gOC total DDx. However, a RG of 400 µg/gOC for total DDx is higher than the RG range derived for the protection of benthic invertebrates and fish, i.e., 50 to 160 µg/gOC (see Sections 2 and 3). The cancer risk associated with the high end of this ecological-based RG range (a total DDx RG of 160 µg/gOC) is 4 x 10^{-5}, which is well within USEPA's acceptable risk range. Thus, a total DDx concentration range of **40 to 160 µg/gOC** is identified as the range of risk-based concentrations for protection of human health that is also consistent with the RGs for ecological receptors. This range equates to 0.4 to 1.6 mg/kg for sediment containing 1% organic carbon, and 2 to 8 mg/kg for sediment containing 5% organic carbon. Like the risk-based concentrations for protection of fish, the concentrations derived for protection of human health are applicable to surface-weighted average DDx concentrations in site sediment following remediation and do not represent not-to-exceed values for individual samples.

6 Precedents from Other Sediment Remediation Sites

Sediment cleanup goals developed for DDx, lead, and arsenic were compiled from the Major Contaminated Sediment Sites (MCSS) Database and the Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) Public Access Database. A summary of these site-specific cleanup goals is provided in Tables 6-1 through 6-3. As indicated on Tables 6-1 through 6-3, remedial goals for DDx range from 0.003 to 94 mg/kg; remedial goals for lead range from 5 to 35,000 mg/kg; and remedial goals for arsenic range from 0.0004 to 317 mg/kg. In comparison with the range of RGs presented in Sections 2 through 5, this review confirms that the conservative RGs identified for the site are within the range of remedial goals approved at other sites. Further interpretation of the remedial goals for these other sites would require a review of the underlying studies that were used to set these goals. Such an assessment is not warranted, as the RGs presented for the Delaware Valley Works site are conservative for this site setting.

7 Conclusions and Recommendations

The literature review and analysis presented in this report support the following risk-based RGs for total DDx, arsenic, and lead in sediment for the protection of human and ecological receptors:

Chemical	RG Range	Controlling Endpoint(s)
Total DDx (µg/gOC)	40-160	Benthic invertebrates, fish, humans
Arsenic (mg/kg)	130-170	Benthic invertebrates
Lead (mg/kg)	150	Fish

These RGs represent a conservative selection of risk-based values for the protection of human and ecological receptors; these values do not incorporate site-specific information on chemical bioavailability and bioaccumulation, which would likely result in higher RGs. However, the calculated values are reasonably conservative and should be considered acceptable to establish the limits for the proposed nearshore sediment remedy.

Figures 7-1 through 7-3 show total DDx, arsenic, and lead concentrations in site sediment samples. Comparisons to the RGs presented above are indicated by the color of the sample location symbols. In assessing the proposed limits of remediation presented to USEPA on February 15, 2011 (see Appendix C), the measured sediment concentrations are evaluated relative to these RGs, as follows:

- Based on the studies presented herein, the low end of these conservative RG ranges should not be interpreted to be not-to-exceed values, as there is substantial information to warrant consideration of acceptable remedial goals within or above this range when site-specific factors are considered.

- The risk-based concentrations for fish and human health apply to average sediment concentrations within the site, while the risk-based concentrations for benthic invertebrates apply at a smaller scale due to the low mobility of many invertebrate species. Therefore, with the exception of RGs based on the protection of benthic organisms, the need for remediation should be based on a comparison of average nearshore sediment concentrations to these goals.

- To develop a reasonably conservative remedy, locations exhibiting sediment concentrations exceeding the RGs will be included within the limits of the remedy footprint and reviewed for the adequacy of delineation.

In consultation with the USEPA, it has been determined that adjusted RGs are appropriate for the limited area of sediment within the drainageway located north of SWMU 9 which discharges into the Delaware River area of interest, and which may potentially be impacted by sediment migration from the Delaware River shoreline. Adjusted RGs for this drainageway are presented in Appendix D.

As shown in Appendix C, the proposed remedy footprint includes sample locations SE-01 through SE-9, SE-11, SE-15 through SE-17, SE-22, and SE-23. At all of these sample locations, sediment arsenic, lead and/or total DDx concentrations are within or above the RG ranges presented above. Among locations along the outer edge of the sampled area, sediment arsenic and total DDx concentrations in the vicinity of sample locations SE-11, SE-15, SE-16, and SE-17 are higher than the low end of the RG range presented above, although the concentrations at SE-15 and SE-16 are within the RG range. Therefore, the results of this comparison of RGs to the proposed remedy limits support the limits of the remedy. Additional sampling to confirm the concentrations measured at locations SE-6 and SE-22 and/or to delineate the extent of RG exceedances in the vicinity of these locations may be conducted as part of the remedy design.

Further, for the purpose of defining the remedy limits, delineation of DDx, lead and/or arsenic concentrations in surface sediments in the vicinity of location SE-11 and SE-17 is proposed, as concentrations at this location exceed the high end of the conservative range of RGs and have not been fully delineated. This work will include the collection of surface sediment samples as follows:

<u>SE-11 Delineation Plan for Arsenic</u>:

- approximately 10-, 20- and 30-feet southeast of location SE-11; and
- approximately 10-, 20-, and 30-feet south of location SE-11.

<u>SE-17 Delineation Plan for Arsenic, DDx and Lead</u>:

- approximately 10-, 20- and 30-feet southeast of location SE-17;
- approximately 10-, 20-, 30-feet south of location SE-17;
- approximately 25-, 50- and 75-feet between SE-17 and SE-22; and
- approximately 25-, 50- and 75 feet between SE-17 and SE-18.

Samples will be collected and analyzed in accordance with the procedures used for the prior sediment sampling events. Samples collected closer to location SE-11 and SE-17 will be analyzed first for comparison with the RGs; remaining samples will be released for analysis based on the results of this comparison.

Following implementation of the proposed nearshore remedy including coverage of locations SE-6 and SE-22, the average concentrations in the nearshore area would be below the RG ranges. Considering the locations outside the remedy footprint (SE-12, SE-13, SE-14, SE-18, SE-19, SE-20, SE-21), the average concentrations are 17.5 µg/gOC (total DDx), 50 mg/kg (arsenic), and 75 mg/kg (lead).[5] Post-remedy average concentrations will be even lower than these levels, when considering that the remediated area would represent non-detectable or naturally occurring background levels of these constituents. Thus, the average remaining delineated concentration would be well below the most conservative RGs, and therefore, the proposed remedy area achieves an acceptable level of risk reduction.

[5] The 95% upper confidence limits of the mean concentrations are 24 µg/gOC (total DDx), 72 mg/kg (arsenic), and 97 mg/kg (lead).

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